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Biodiesel fuel from rapeseed oil as prepared in supercritical methanol

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Abstract

Transesterification reaction of rapeseed oil in supercritical methanol was investigated without using any catalyst. An experiment has been carried out in the batch-type reaction vessel preheated at 350 and 400°C and at a pressure of 45–65 MPa, and with a molar ratio of 1:42 of the rapeseed oil to methanol. It was consequently demonstrated that, in a preheating temperature of 350°C, 240 s of supercritical treatment of methanol was sufficient to convert the rapeseed oil to methyl esters and that, although the prepared methyl esters were basically the same as those of the common method with a basic catalyst, the yield of methyl esters by the former was found to be higher than that by the latter. In addition, it was found that this new supercritical methanol process requires the shorter reaction time and simpler purification procedure because of the unused catalyst. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Supercritical methanol; Methyl esters; Biodiesel

1. Introduction

As energy demands increase and fossil fuels are limited, research is directed towards alternative renewable fuels. Biomass has been found to produce low-molecular-weight organic liquids, which can be used or proposed for vehicles. A potential diesel oil substitute is biodiesel, consisting of methyl esters of fatty acids produced by the transesterification reaction of triglycerides of vegetable oils with methanol with the help of a catalyst [1]. Due to the great molecular similarities of biodiesel to parafinic diesel fuel compounds, this alternative fuel has a chance of fulfilling the demands that diesel engine makes of its fuel. Essentially, no engine modifications are required to substitute biodiesel for diesel fuel that can maintain the engine performance. In addition, biodiesel is better than diesel fuel in terms of sulfur content, flash point, aromatic content and biodegradability [2].

For this biodiesel fuel, there have been various studies in Europe, US and Japan and most of the conventional methods for biodiesel production use a basic or acidic catalyst. With an acid catalyst, a reaction of 1–45 h was necessary for the formation of the respective esters and by basic catalyst, it is somewhat faster depending on the temperature and pressure, but it still takes 1–8 h for a reaction [3–8]. The reaction is initially slow because of the two-phase nature of the methanol/oil system, and slows even further because of polarity problem [8]. In addition, a removal of both the catalyst and the saponified products after the reaction is essential for its purification [9].

It is, thus, of great interest from a practical point of view to study a practically possible process without using any catalyst. In this work, therefore, we have made a fundamental study on the transesterification of the rapeseed oils in supercritical methanol to investigate the possibility of converting the triglycerides of the rapeseed oil to methyl esters as biodiesel fuels [10].

2. Materials and methods

The rapeseed oil from Nacalai Tesque was used in this work as a vegetable oil. In addition, various methyl esters such as palmitic, stearic, oleic, linoleic and linolenic acids were obtained from Nacalai Tesque as a standard.

The supercritical methanol biomass conversion system employed in this work is shown in Fig. 1. The 5 ml reaction vessel made of Inconel-625 was used in this system in which the pressure and temperature were monitored in a real time, covering up to 200 MPa and 550°C, respectively. The reaction vessel in this system was charged with a given amount of rapeseed oil (2.00 g) and liquid methanol (3.36 g) with a molar ratio of 1:42. The reaction vessel was then quickly immersed into the tin bath preheated at 350 or 400°C, and kept for a set time interval for supercritical treatments of

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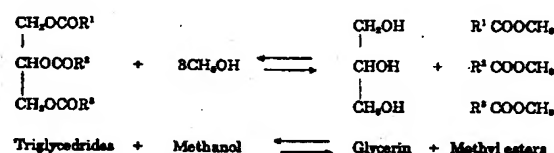*E-mail address:* saka@energy.kyoto-u.ac.jp (S. Saka).

methanol, from 10 to 240 s. It was, subsequently, moved into the water bath to stop the reaction.

The treated rapeseed oil was then allowed to settle for about 30 min to have the three phases separated. The top phase consisting of methanol was then removed, and for the remaining phases, the upper and the lower, each portion was evaporated at 90°C for 20 min to remove the remaining methanol. After measuring their residual weight, the upper and the lower portions were analyzed for its composition by using the high performance liquid chromatography (HPLC) (Shimadzu, LC-10AT) which consists of the column (STR ODS-II, 25 cm in length × 4.6 mm in inner diameter, Shinwa Chem. Ind. Co.) and refractive index detector

Ford Development Ltd, Japan and Bio Super 300 from VOGEL and NOOT Technology, Biodiesel International, Austria. The former was produced from the wastes of the rapeseed oil, whereas the latter is from virgin rapeseed oil.

3. Results and discussion

Assuming that the transesterification reaction of the rapeseed oil in the supercritical methanol proceeds under the same reaction mechanism as that of using liquid methanol, the reaction proceeds without any catalyst as follows:

$$
\begin{array}{ccc}
CH_2OCOR^1 & & CH_2OH \qquad R^1COOCH_3 \\
| & & | \\
CHOCOR^2 & +\ 3CH_3OH \rightleftharpoons & CHOH \ +\ R^2COOCH_3 \\
| & & | \\
CH_2OCOR^3 & & CH_2OH \qquad R^3COOCH_3
\end{array}
$$

$$\text{Triglycerides} + \text{Methanol} \rightleftharpoons \text{Glycerin} + \text{Methyl esters}$$

(Shimadzu, RID-10A) operated at 40°C with 1.0 ml/min flow rate of methanol as a carrier solvent. The sample injection volume was 20 μl and the peak identification was made by comparing the retention time between the sample and the standard compound.

For comparison, common methylesterification reaction of the rapeseed oil was made with liquid methanol and a catalyst of sodium hydroxide at 60°C in an ordinary pressure. The obtained methyl esters as well as commercial biodiesel oils were then analyzed by the HPLC. The commercial biodiesel oils studied are E-Oil from Lon

where R^1, R^2 and R^3 are alkyl groups with chain lengths ranging mainly from C_{11} to C_{17} [11],[12]. Theoretically, transesterification reaction is equilibrium reaction. In this reaction, however, more amount of methanol was used to shift the reaction equilibrium to the right side and produce more methyl esters as the proposed product.

Fig. 2 shows a typical example of the relationship between the reaction time and the temperature and pressure in the reaction vessel as immersed into the tin bath preheated at 400°C. It is clear that it takes about 11 s to reach the supercritical methanol (SC MeOH) conditions in which the critical temperature and the critical pressure of methanol are, respectively, 239°C and 8.09 MPa. However, once the reaction vessel was immersed into the water bath, the supercritical conditions were released to the ordinary conditions in a few seconds.

With this biomass conversion system, the rapeseed oil was treated in supercritical methanol at a preheating temperature of 350°C. The maximum temperature and pressure reached were 342°C and 45 MPa. The treated oil was studied for its upper and lower portions by the HPLC. The HPLC chromatogram obtained for the lower portion, which contains heavy glass clear liquid, is shown in Fig. 3. From the chromatogram of the glycerin standard shown, the liquid obtained in the lower portion can be glycerin, as expected.

For the upper portion, the obtained HPLC chromatograms are shown in Fig. 4. Methyl esters of the rapeseed oil are known to consist of methyl palmitate ($C_{16:0}$), methyl stearate ($C_{18:0}$), methyl oleate ($C_{18:1}$), methyl linoleate ($C_{18:2}$) and methyl linolenate ($C_{18:3}$), in which the first number in the subscript is that of carbons in the alkyl chain, while the second is that of the double bond [13]. These methyl esters
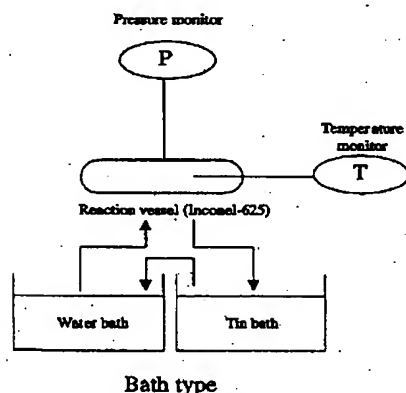

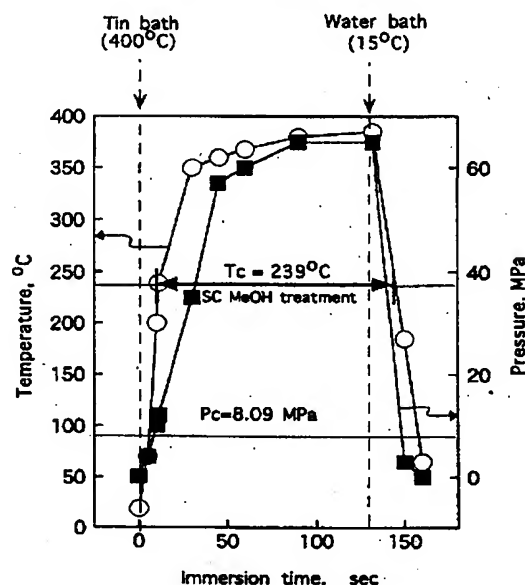Fig. 1. Supercritical methanol biomass conversion system.

Fig. 2. Temperature and pressure curves of the 5 ml reaction vessel containing methanol. Temperatures of the tin bath and water bath are 400 and 15°C, respectively.

studied by the HPLC. appear in the retention time less than 10 min in the chromatograms, while the peaks at the longer retention times observed are believed to be partially methylated esters such as diglycerides and monoglycerides. As transesterification proceeds, the peak intensities of methyl esters are apparently increased with a decrease in those of partially methylated esters.

The changes in the transesterification products are shown in more detail against the supercritical treatment in Fig. 5. The course of the reaction is fast in the beginning and gradually becomes slow in the longer reaction time. Except for methyl linolenate, the volumetric concentration of methylated compounds increases in line with the reaction time. The reason for a trend of methyl linolenate is not known, but from an examination on free fatty acids of rapeseed oil [15], it was found that linolenic acid is the fastest to be methyl esterified followed by linoleic and oleic acids which have less double bonds than linolenic acid. Furthermore, the ester of linolenic acid is most unstable against higher temperature treatment. Therefore, the volume percentage of methyl linolenate would be decreased in the later stage of the treatment as shown in Fig. 5. This further implies that the volume
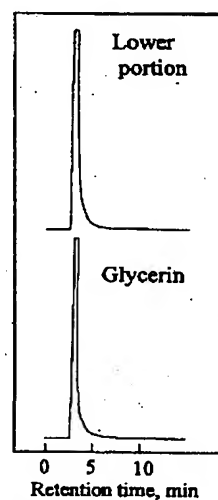

Fig. 3. HPLC chromatograms of the lower portion as rapeseed oil treated with supercritical methanol at 350°C.
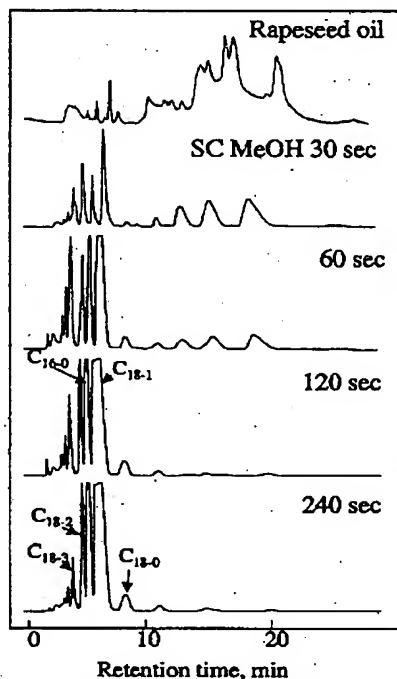
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Fig. 4. Changes in HPLC chromatograms of the upper portion as rapeseed oil treated with supercritical methanol at 350°C as a function of reaction time.

Table 1
Comparison in the yield of methyl esters and glycerin in the upper and lower portions between the supercritical methanol method and the common method

Methods	Upper portion (g)	Lower portion (g)
SC MeOH method	1.98	0.23
Common method	1.95	0.23
Theoritical value	2.01	0.23

percentage of methyl esterified compounds may depend to some extent on the treatment condition applied. For a treatment of 350°C and 120 s, methyl oleate shares the biggest portion in the methylated compounds followed by methyl palmitate, methyl linoleate, methyl linolenate, and the last being methyl stearate.

It is interesting to note from Fig. 5 that over 40% of the rapeseed oil is methyl esterified only at 30 s treatment and that 240 s supercritical treatment has resulted in over 95% conversion to methyl esters. This result is significant when compared with the other previous results. Diasakov et al. [14], have reported that without a catalyst, methyl esterification of soybean oil required 10 h to get 85% yield at 235°C, while Marinkovic [3] reported to need 3 h to yield the same result by using an acid catalyst.

Fig. 6 shows a direct comparison in the HPLC chromatograms between the supercritical methanol-treated sample at a preheating temperature of 350°C (240 s) and that prepared

by the common method which employs a catalyst of sodium hydroxide. For comparison, also shown is the chromatogram of the rapeseed oil treated in the higher preheating temperature of 400°C (120 s) with supercritical methanol. The E-Oil and Bio Super 3000 are both commercially available biodiesel fuels produced from the wastes of the rapeseed oil and virgin rapeseed oil, respectively, with a basic catalyst. It is clear from these chromatograms that the patterns of the common method and the commercial fuels are similar to each other. However, supercritically treated sample at 400°C is somewhat different, particularly in the shorter retention times of the chromatogram. This difference is clearly demonstrated in Fig. 7 in which its sample contains more methyl linoleate and metyl linolenate, while the other three oils are higher in the content of methyl oleate. The reason for this would be related with the supercritical condition in which higher temperature and pressure of the reaction were employed. As mentioned previously, the rate of decomposition and dehydrogenation reactions might be higher at longer treatment and higher temperature treatment in the following order of methyl linolenate, methyl linoleate and methyl oleate. In consequence, part of methyl esters with less double bonds would be converted to compounds with more double bonds as observed in the shorter retention time of the HPLC chromatograms. The rapeseed oil treated in 350°C of supercritical methanol for 240 s showed a comparable methyl esters composition with that of three other oils. In addition, the non-methyl esters are more or less the same in content. It can be, therefore, proposed that the transesterification reaction is more suitable at a temperature of 350°C, while at 400°C, the dehydration reaction proceeds perhaps with some fatty acids at the same time with transesterification reaction of the rapeseed oil.

Table 1 shows the yields of methyl esters and glycerin in the upper and lower portions as the rapeseed oil was treated in supercritical methanol. For comparison, the yields by the common method and their theoretical values are also included. The yield of the upper portion consisting of methyl esters prepared by this supercritical methanol method is even higher than that of the common method. The increased yield in this supercritical process would be due to a conversion of free fatty acids to its methyl esters. Free fatty acids, which are converted in the common method to be the saponified products by the alkaline catalyst, were recently found to be converted to

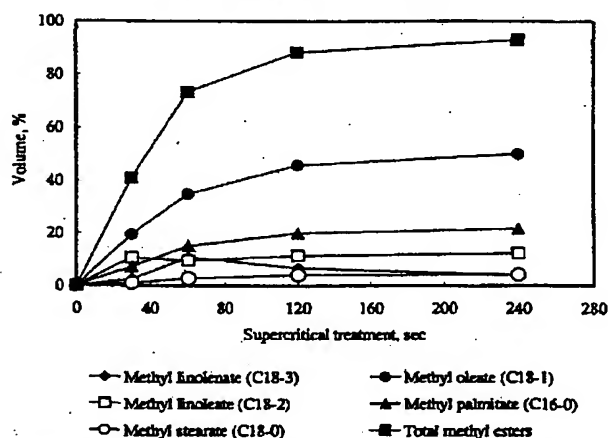S. Saka, D. Kusdiana / Fuel 80 (2001) 225–231　　　　　229

Fig. 5. Changes in volume percentage of methyl esters as treated with supercritical methanol at 350°C as a function of reaction time.

methyl esters through the dehydration reaction during the supercritical treatment of methanol as published elsewhere [15]. This finding suggests that the supercritical methanol treatment has a great availability to perform the transesterification reaction, and that it would provide a clue as to establishing a new process for converting vegetable oil to biodiesel fuel.

As it was already mentioned, biodiesel production by the common method requires a catalyst, either basic or acidic. The schematic of its process is shown in Fig. 8. Generally, methyl esterification reaction takes place in the elevated temperature around 60°C and post treatment becomes crucial because several steps of purification are needed to achieve methyl esters from the upper portion. For the lower portion, it is necessary to remove all the saponified products produced from free fatty acids and basic catalyst to achieve glycerin, as co-products. The supercritical methanol process, however, becomes much simpler as in Fig. 9, since it is a catalyst-free process and thus only a removal of methanol is required.

The common method employed for the commercial production of methyl esters takes 1–8 h at a temperature close to 60°C. The reaction is initially slow because of the two-phase nature of the methanol/oil system, and slows even further because of the polarity problem even with the help of an acid or an alkali catalyst. However, as described in this work, supercritical method can readily solve these problems because of the supercritical temperature and pressure employed. The dielectric constant of liquid methanol which tends to be decreased in the supercritical state increases the solubility of oil in methanol to form a single phase of methanol/oil system. Solubility parameter of the rapeseed oil determined by the theoretical calculation is about 18 (MPa)$^{1/2}$ while methanol is 26 (MPa)$^{1/2}$ and its value decreases to be closer to that of the rapeseed oil in supercritical state depending on the temperature and pressure employed [16]. It was also reported by Ma [4] that the solubility of triglycerides in methanol increased at a rate of 2–3% (w/w) per 10°C as the reaction temperature increased. In addition, a kinetic study clearly indicated that the reaction rate

Table 2
Comparison between the common method and the supercritical methanol method for biodiesel production

	Common method	SC MeOH method
Reaction time	1–8 h [3–5]	120–240 s
Reaction conditions	0.1 MPa, 30–65°C [4]	>8.09 MPa, >239.4°C
Catalyst	Acid or alkali [3,4]	None
Free fatty acids	Saponified products	Methyl esters
Yield	Normal	Higher
Removal for purification	Methanol, catalyst and saponified products	Methanol
Process	Complicated	Simple

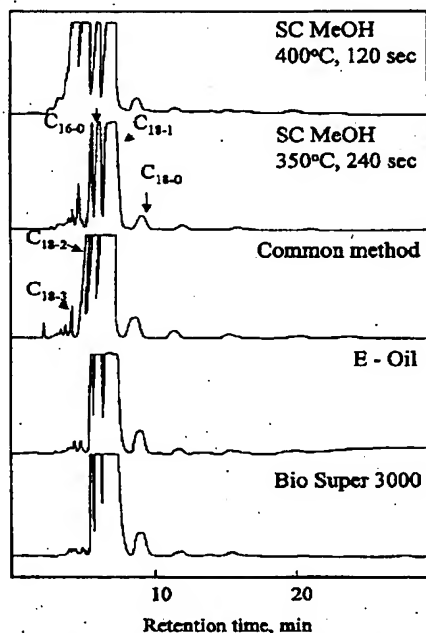230　　　　　　　　　　　*S. Saka, D. Kusdiana / Fuel 80 (2001) 225-231*

Fig. 6. HPLC chromatograms of methyl esters prepared by supercritical methanol and common method, compared with those of commercial biodiesel oils.
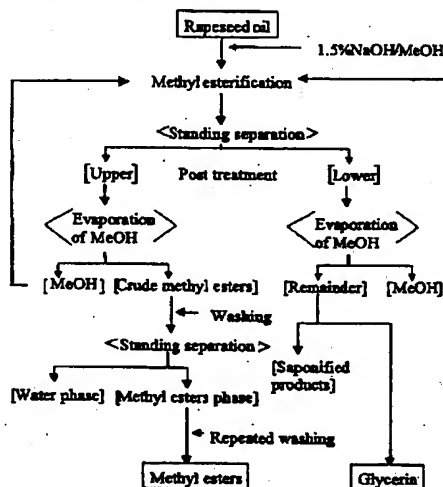

Fig. 8. Schematic process of the commercial biodiesel fuel production by the common method.

constant in transesterification is greatly increased in the supercritical state [15]. Consequently, the reaction can be completed in a very short time.

In conclusion, Table 2 summarizes the superiority of the supercritical methanol process over the common method. The merit of this method is that this new process just requires a very short reaction time. In addition, because of the non-catalytic process, the purification of products after transesterification reaction is much simpler and environ-
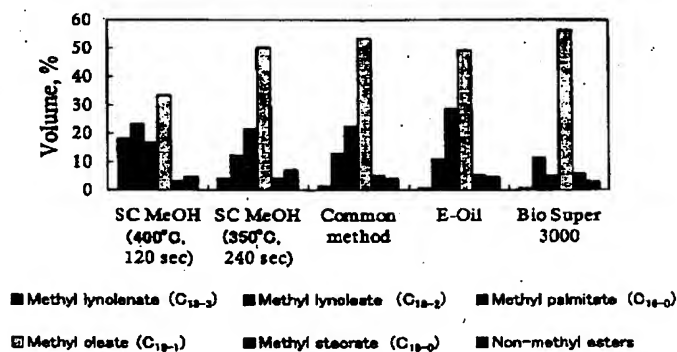

Fig. 7. Volume percentage of methyl esters and non-methyl esters of supercritically prepared biodiesel oil, compared with those of commercial biodiesel oils.
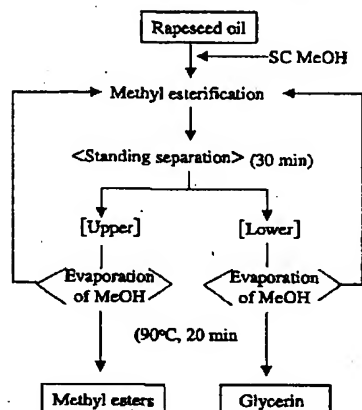
Fig. 9. Schematic process of biodiesel fuel production by supercritical methanol.

mental friendly, compared with the common method in which all the catalyst and saponified products have to be removed for biodiesel fuels. As a result, it just needs less energy for the manufacturing process. Therefore, this new process can offer an alternative way to convert vegetable oils to methyl esters by a simpler–safer–shorter production process in an environmental friendly manner.

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